Femtosecond solvation dynamics of hydrogen-bonding complexes

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1. INTERMOLECULAR HYDROGEN-BONDING INTERACTIONS

Hydrogen-bonds are among the most common chemical interactions in condensed phases [1-3]. Some notable examples for the importance of the hydrogen-bonding interactions are the physical properties of liquid water and ice which are largely determined by the extensive hydrogen-bond network existing in bulk water, bimolecular proton-transfer reactions which usually proceed along one or several hydrogen-bonds connecting between the proton donor (acid) and the proton acceptor (base) and the 3-D structure of large biomolecules such as the DNA molecule, which are stabilized by specifically “engineered” hydrogen-bonding interactions.

Hydrogen-bonds also consist an important part of solute-solvent interactions in solution [4, 5]. These interactions are usually referred to as “specific” solute-solvent interactions. The terminology is used to distinguish between hydrogen-bonding interactions which are short-range and solute-solvent interactions originating with the dielectric properties of the solvent which are long-range compared to the molecular graining of the solvent.

In this study we focus on the dynamic aspects of the hydrogen-bonding interaction of some hydroxy-photoacids (ROH) [6]. By optically exciting the photoacid, we have induced a sudden increase in the acidity of the OH group. The enhanced acidity has caused a sudden increase in the hydrogen-bonding interactions of the photoacid usually of the type O–H⋯O. The hydrogen-bonding complex (ground-state) of the photoacid was prepared in solutions of the photoacid in non-polar solvents and in presence of suitable complexing oxygen bases such as DMSO.

There have been several experimental observations indicating that the response of an existing hydrogen-bond interaction to a sudden change in its interaction potential is ultrafast [7, 8]. In particular, a recent observation by Rini et al. [9] has demonstrated that bimolecular proton transfer along an existing hydrogen-bond may be faster than 150fs when the proton transfer is between a strong photoacid directly hydrogen-bonded to a strong base. The question rises, then, does such an ultrafast proton transfer reaction proceeds before the hydrogen-bond connecting the acid and base relaxes to its new equilibrium ‘bond’ length following the optical excitation of the photoacid? In such a case, the relevant time-scale for bimolecular proton-transfer along a pre-existing hydrogen-bond may be as fast as the stretching period of the O–H bond (ca. 10fs). However, if the heavy atom distance (O⋯O) needs to relax prior to the proton transfer reaction, than the proton transfer rate may be limited by the relatively slow hydrogen-bond dynamics (typically about 100fs).

2. THE TIME-RESOLVED STUDIES OF HPTA-DMSO COMPLEXES IN DCM SOLUTIONS

A direct estimation of the O⋯O time-response following the optical excitation of a strong photoacid, 8-hydroxypyrene 1,3,6 tris-dimethylsulfonamide (HPTA), is reported below. Fig. 1a
shows the large effect on the optical spectra of HPTA of adding small amounts of a weak oxygen-base, DMSO, to solutions of HPTA in dichloromethane (DCM).

![Spectra Diagram](image)

**Fig. 1.** Fluorescence and absorption spectra of HPTA (1a) and MPTA (1b) in pure DCM – solid lines and in DCM in the presence of 10^{-2} M DMSO – dashed lines.

In contrast, practically no effect was observed when DMSO was added to solutions of MPTA, the methoxy analogue of the photoacid, where the acidic hydrogen atom of the photoacid was replaced by a methyl group (Fig. 1b).

Fig. 2 shows the effect of creating hydrogen-bonding complexes between HPTA and oxygen-bases on the solvation correlation function of HPTA, C(t) [10]. Utilizing a pump-probe set-up described elsewhere [11], with 400 nm excitation, the dynamic stokes shift of HPTA was analyzed with about 50fs time-resolution. The hydrogen-bonded HPTA exhibited much faster dynamics than the solvation dynamics of the uncomplexed HPTA in pure DCM.

![Correlation Function Diagram](image)

**Fig. 2.** Plots of calculated C(t) (a) of 5×10^{-4} M HPTA in pure DCM (circles), (b) in presence of 9×10^{-3} M DMSO (triangles) and (c) in presence of 0.1M dioxane (squares). Parameters of the fits, (solid lines) are shown in Table 1.
The detailed comparison between the C(t) of uncomplexed HPTA and the C(t) of complexed HPTA (Table 1) shows that the dynamics of the hydrogen-bonded HPTA contain an additional sub-100fs component over the solvation dynamics found in the pure solvent.

Table 1.
Parameters for the multiexponential fit of C(t), C(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3), of HPTA in various solutions.

<table>
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<th>DCM</th>
<th>DCM+9x10^{-3} M DMSO</th>
<th>DCM+0.1 M dioxane</th>
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<tr>
<td>A_1 (%)</td>
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<td>15</td>
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<tr>
<td>\tau_1 (fs)</td>
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<td>56</td>
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<td>A_2 (%)</td>
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<td>A_3 (%)</td>
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<td>\tau_3 (ps)</td>
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A reconstruction of the measured time-dependent absorption spectra of the hydrogen-bonding complexes of HPTA with DMSO in DCM is shown in Fig. 3 as the superposition of the absorption and the gain bands of the photoacid.

![Fig. 3. Reconstruction of the transient absorption spectra of HPTA in DCM in the presence of 9x10^{-3} M DMSO at different pump-probe delays. The time-zero absorption and gain bands of the photoacids are moving toward each other following the relaxation of the solute-solvent interactions to their steady-state values. Full lines are the superposition of the individual absorption and gain bands of HPTA.](image)

We conclude that the additional (over the solvation dynamics in the pure solvent) sub-100fs transient observed in the C(t) of the hydrogen-bonding complexes of HPTA is due to transient changes in the hydrogen-bonding complexes of the type portrayed in Fig. 4 [1, 12]. The time scale is that of the heavy-atom movement within the O–H···O (hydrogen) bond. It resembles, yet it is faster than, the inertial response of the solvent [12-23].

It appears that hydrogen-bonds are potentially fast enough so to allow for bimolecular proton-transfer to occur along relaxed hydrogen-bond links, thus making the preparation of such links, which may involve relatively slow solvent fluctuations, the primary event that establishes the proton transfer coordinate.
Fig. 4. (a) Schematic response of the covalent O–H bond to the optical excitation of the hydrogen-bonded photoacid. The relaxed state of the hydrogen-bonded photoacid has a (slightly) longer O–H bond-length and a smaller zero-energy value than the locally excited state [24]. (b) Schematic response of the OH···O bond to the optical excitation of the hydrogen-bonded photoacid. $E^+_{HB}$ and $E^0_{HB}$ are the hydrogen-bond interaction energy in the ground-state and the excited-state of the photoacid, respectively, the excited-state interaction being larger. The arrows symbolize the optical transitions.

REFERENCES